# Molecular Size and Solvation of Low Molecular Weight Poly(ethylene Oxide) and Phenol–Formaldehyde Resols in Different Solvents

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## Synopsis

Several solvent systems are presently used to characterize the molecular weight of phenol–formaldehyde resins. However, results reported in the literature for different molecular weights may not be representative of true molecular weight, but rather may be distorted by aggregation and solvation. In this report an effort to clarify this situation was conducted, first by using a suitable calibration with poly(ethylene glycol) and then using this polymer as a molecular size standard to determine the size of phenol–formaldehyde oligomers in solution. In the calculation of the molecular sizes of phenol–formaldehyde resols, proper accounting of the variation of the Mark–Houwink parameters with molecular weight for low degrees of polymerization must be made for poly(ethylene glycol). The Mark–Houwink constants for poly(ethylene glycol) are very similar in presence or absence of salts, and are considered to be unaffected by solution ionic strength. It is not the case for phenol–formaldehyde, whose apparent molecular size varies with the nature of the solvent. The actual molecular weight and molecular dimension distribution are discussed for different type A resols used as adhesives in the wood composite industry.

## INTRODUCTION

Several solvent systems are used to characterize the molecular weight (MW) of phenol–formaldehyde (PF) resins. Results reported in the literature may not be representative of true molecular weight, but are distorted by aggregation and solvation.[1,2] This is also true for lignin, the naturally occurring polymer, which is a partially degraded (when solvated), crosslinked polymer,[3] polyacrylonitrile,[4] and other polymers.[5] We wish to report on an effort to clarify this situation, by using suitable calibrations with low molecular weight poly(ethylene oxide), also known as poly(ethylene glycol) or PEG. This polymer was used as a molecular size standard to determine the size of PF molecules in solution in the presence of salts. PEG was chosen as the reference polymer since very low molecular weights are available: however, proper care must be taken in establishing the molecular weight-intrinsic viscosity (log–log) curve, since it is nonlinear, especially at low molecular weights. This calibration must be conducted for each solvent system characterized, as the use of Mark–Houwink (MH)[6] parameters $K$ and $\alpha$ only is not accurate enough at low molecular weights.

The use of solvent with adjusted ionic strengths have been useful in measuring the molecular weight distribution of aggregating polymers in solution.[5] In general the effect of salts (ionic strength) on the solvation of PEG is limited, as is indicated by the similarity of MH parameters[6] in tetrahydrofuran (THF), $n,n$-dimethylformamide (DMF), and water, on the one hand, and, on the other hand, as will be shown, ionic solutions such as THF with 0.4% trichloroacetic acid (TCAA), DMF with $0.1M$ lithium chloride (LiCl), and water–borax–NaOH (pH 10) buffer. These solvent/cosolvent systems were chosen for their ability to solubilize resols.[7-9] For the resols, the molecular solvation in these different solvent systems is quite different, as will be shown. The determination of the intrinsic viscosity and the value of the MH constants for PEG is required to determine the molecular size distribution of the resols, and to help determine the degree to which aggregation or association in solution exists.

To compare the performance of different columns/solvent systems, it is especially convenient to convert MW distributions to ($[\eta]*M$) distribution and averages, where $M$ is the molecular weight, $[\eta]$, the intrinsic viscosity and ($[\eta]*M$) corresponds to molecular size. Rudin and Hoegy[10] showed that universal calibration is possible for relatively low molecular weights without correction for concentration effects. It is then possible to obtain molecular weight averages as well as molecular size averages in the aforementioned solvents. If there is no aggregation, the calculated molecular weight and size distribution of two resols should give the same averages as the experimentally determined distribution for the mixture of both.

The aim of such research is to characterize in a nonambiguous manner the molecular size distribution of resols used as adhesives in the wood composite industry and to eventually correlate these data with kinetic, spectroscopic, and mechanical results to obtain better, low-cost resol systems. For instance, it is not known which molecular size distribution of resol provides the best adhesive properties when used alone or combined with specific wood waste extenders or the relationship between molecular size distribution and the curing parameters.

## EXPERIMENTAL

Detailed descriptions of the size-exclusion chromatography (SEC) columns and solvent systems used to characterize the resols are given in Ref. 11. In summary, size exclusion chromatography was conducted on phenol–formaldehyde resols, with prior PEG calibration on the following column/solvent systems: (1) Ultrastyragel (Waters) 100 and 500 Å columns in series at 25°C with THF/0.4% TCAA as solvent, (2) PLgel (Polymer Laboratories, U.K.) 50 and 500 Å columns in series with DMF as solvent at 25°C, and (3) same as (2) with DMF/$0.1M$ LiCl as solvent at 25 and 85°C. Once the columns have been exposed to high ionic strength solvents, it has been found out that it is best not to return the columns to pure solvents, since the nonmobile phase is sensitive to ionic strengths changes, i.e., these columns should be kept for SEC of resols. Measurements were also made with Ultrahydrogel (Waters) 120 and 500 Å columns in series with water–borax–NaOH pH 10 buffer[12]; however, the resulting SEC spectra were indicative of an interference due to specific
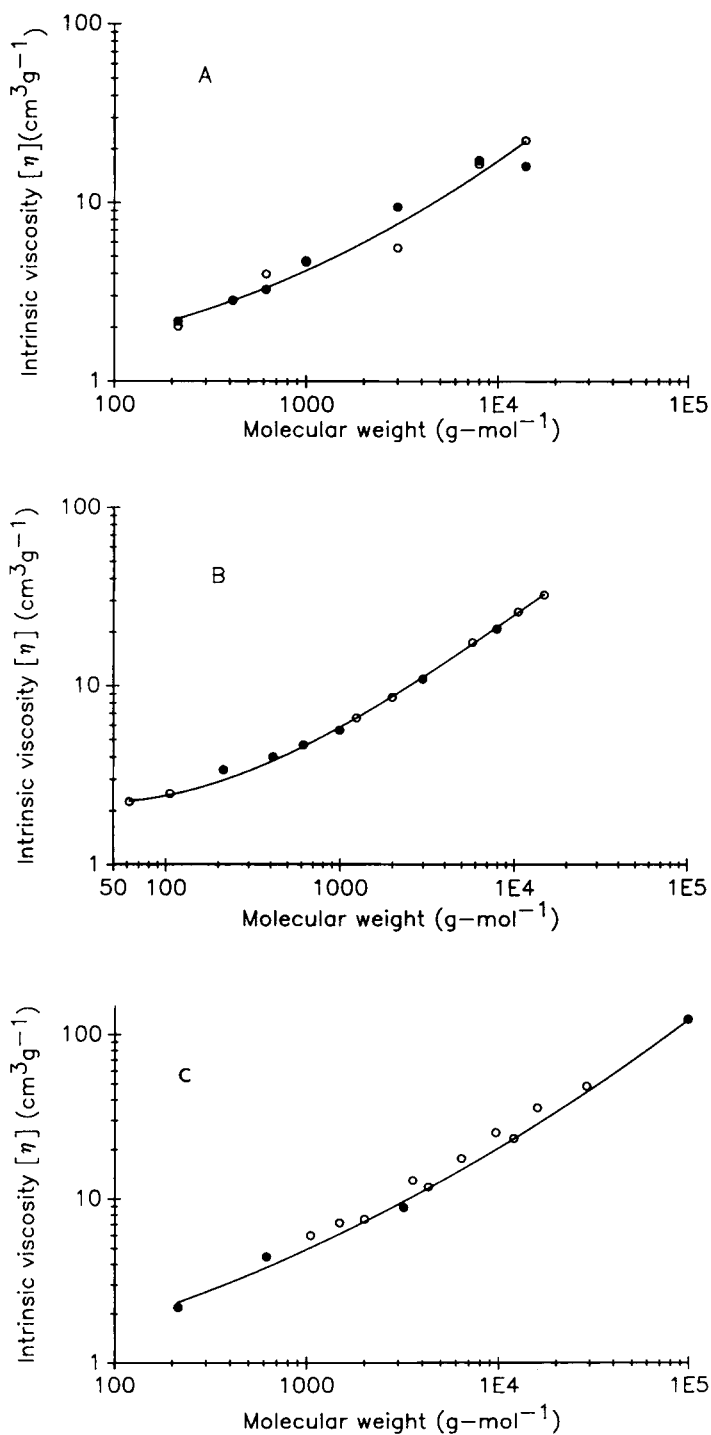
Fig. 1.   Intrinsic viscosities $[\eta]$ of poly(ethylene glycol) as a function of the weight average molecular weight for the different solvent systems: ($\bigcirc$) in the pure solvent; ($\bullet$) in mixed solvent. (A) Tetrahydrofuran and tetrahydrofuran with 0.4% trichloroacetic acid; (B) water[14] and water–NaOH pH 10 buffer; (C) $n,n$-dimethylformamide and $n,n$-dimethylformamide with $0.1M$ lithium chloride.

| Solvent system | $A$ $K^{a}$ ($cm^3$ $g^{-1}$) | | $\alpha^{a}$ | $A^{b}$ | $B^{b}$ | $C^{b}$ | Number of data points[c] |
|---|---|---|---|---|---|---|---|
| THF, 25°C | 1.4 | 0.020 | 0.73 | 0.265 | −0.251 | 0.123 | 7 |
| THF/TCAA, 25°C | 1.2 | 0.014 | 0.79 | 0.151 | −0.212 | 0.125 | 7 |
| Water, 25°C[d] | 1.5 | 0.029 | 0.72 | | | | |
| Water/borax– NaOH buffer, 25°C | 2.2 | 0.013 | 0.82 | 0.940 | −0.589 | 0.176 | 6 |
| DMF 25°C[e] | 2.0 | 0.024 | 0.73 | | | | |
| DMF/0.1$M$ LiCl, 25°C | 1.2 | 0.032 | 0.70 | −0.165 | 0.036 | 0.083 | 4 |

[a] Calculated from the slope at MW = $10^4$.
[b] Constants of the equation $\log[\eta] = A + B \log(M) + C \log(M)^2$.
[c] For MW range, see Figures 1a–c.
[d] Data from Ref. 14.
[e] Data from Ref. 15.

interactions of the column gel with PF resols and thus were not usable. The experimental setup consisted of a Waters WISP 710B injection system, M45B pump, R401 differential refractometer, and programmable system controller with data module.

The intrinsic viscosities of poly(ethylene oxide) oligomers used were measured in THF, THF/0.4% TCAA, water–borax–NaOH pH 10 buffer and DMF/0.1$M$ LiCl (no measurements were made in DMF/LiCl at 85°C). The weight average molecular weights of the oligomers were, with the polydispersities in parentheses, 215(1.06), 415(1.14), 620(1.18), 1000(1.15), 3000(1.09), 8000(1.58), and 14,000(1.24) as measured with Ultrastyragel (Waters) 100 and 500 Å columns in THF, calibrated with PEG standards (Polymer Laboratories) whose polydispersities were between 1.00 and 1.11. The PEG of molecular weight 100,000 (Polysciences) was used as such. The LiCl (Mallinckrodt) and TCAA (BDH) were reagent grade and the DMF and THF (Aldrich) were HPLC grade.

The viscosities were measured in an Ubbelohde (Industrial Research Glassware Co) viscosimeter at 25°C. The resulting intrinsic viscosities are shown in Figure 1 and the corresponding MH constants in Table I.

## RESULTS AND DISCUSSION

### Poly(ethylene Glycol) Molecular Size in Solution

Poly(ethylene glycol), as several other polymers,[13] does not follow a linear Mark–Houwink relationship, such as

$$[\eta] = K'M^{\alpha} \tag{1}$$

where $K'$ is the Huggins constant, $M$ the molecular weight, and $\alpha$ the exponent (sometimes symbolized as $a$), when the logarithm of the intrinsic viscosity is plotted, as a function of the logarithm of the weight average molecular weight [Figs. 1(a)–1(c)]. Instead, the curve has a distinct upward

concavity at low molecular weights, ie, the Huggins constant $K$ is higher, and the exponent $\alpha$ lower than in the high ($> 1000$) molecular weight linear region.[13-16] In fact, $\alpha$ tends toward 0.5, at very low molecular weights for the ethylene glycol oligomers. The value of the exponent $\alpha$ may even reach 0.5 or a lower value for other polymers, although the oligomer is not in an ideal $\theta$ solvent: This is possible because small chains do not obey the same long range statistics as large chains.[16] Also, branching lowers the value of $\alpha$ in a $\theta$ solvent, (typical value is 0.25 for a highly branched polymer[17]). Low molecular weights resols would be expected to be highly branched since one of the monomers, phenol, is trifunctional.

Sadron and Rempp[18] used the simple empiric equation

$$[\eta] = A + KM^\alpha \tag{2}$$

to represent the variation of $[\eta]$ with MW, for linear low molecular weight polymers, where $A$ is a constant which becomes negligible at high molecular weight. In this particular case, $K$ and $\alpha$ were calculated from the slope and intercept of the curve of the logarithm $[\eta]$ as a function of the logarithm of the molecular weight as expressed in eq. (5) at relatively high molecular weight ($10^4$), and the value of the parameter $A$ was then obtained by least squares from the low molecular weight data. Table I gives the values for $A$, $K$, and $\alpha$ for PEG in THF, water, and DMF: the difference between the MH parameters for these solvents is small in view of the high variation of $K$ and $\alpha$ with solvent nature [and temperature, especially in water[6]] as seen in Figure 2, where $K$ is shown as a function of $\alpha$: This type of representation is called an Elias plot,[6,19,20] where $K$ is seen to be inversely proportional to $\alpha$.
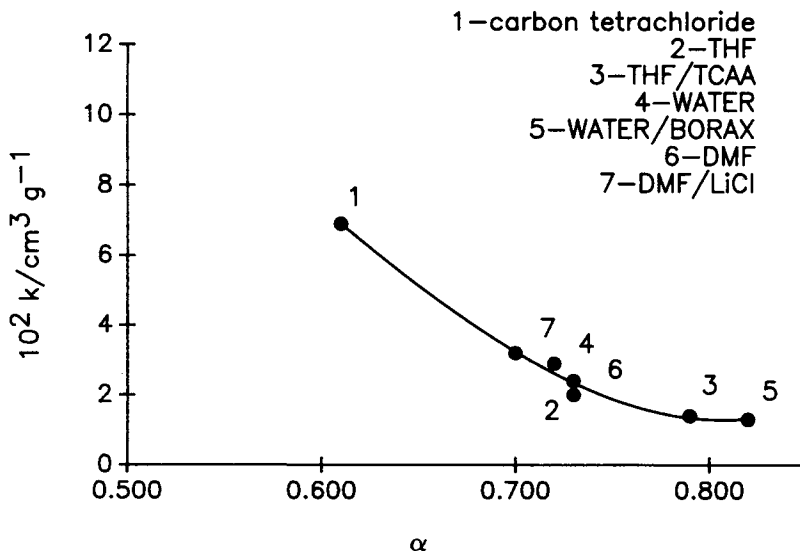


Fig. 2. Mark–Houwink constants $K$ vs. $\alpha$ (Elias plot) for high ($> 1000$) molecular weight poly(ethylene glycol) for the different solvent systems: (1) carbon tetrachloride[18]; (2) tetrahydrofuran; (3) tetrahydrofuran with 0.4% trichloroacetic acid; (4) water[14]; (5) water–NaOH pH 10 buffer; (6) $n,n$-dimethylformamide[15]; (7) $n,n$-dimethylformamide with 0.1$M$ lithium chloride.

Values of 0.12 cm$^3$ g$^{-1}$ for $K$ and 0.5 for $\alpha$ indicate an ideal (e.g., poor) solvent, while values of 0.020 cm$^3$ g$^{-1}$ for $K$ and 0.8 for $\alpha$ indicate a good solvent. Carbon tetrachloride would then be a mediocre solvent and the other afore-mentioned solvents would all be rather good solvents.

The salting out of PEG is related to the order of increased effective hydrated radii,[19] and as such LiCl has very little effect on the LCST of PEG.[19] The effect of TCAA in THF, borax–NaOH in water, and LiCl in DMF on the hydrodynamic volume of PEG is negligible at molecular weights above 10$^4$ and only slight for PEG oligomers [Figs. 1(a)–1(c)]. The addition of TCAA to THF (Fig. 2, points 2–3) and of borax–NaOH (Fig. 2, points 4–5) to water slightly increases the value of $\alpha$, while the addition of LiCl to DMF decreases $\alpha$. As seen in Figure 2, these changes are not very great, compared to the effect of different solvents (CCl$_4$) or temperatures: for instance, $\alpha$ is about 0.81 in water at 45°C.[6]

### Phenol–Formaldehyde Resol Molecular Size in Solution

In the literature, molecular weight distributions for resols are usually expressed in terms of retention times or (occasionally) molecular weights, relative to a calibration polymer.[7–9,21,22] However, PF resols may be swollen in different manners in different solvents according to their interaction with the solvent. Moreover, the polymer used for column calibration will also be affected similarly. In order to take these effects into account, the size of the polymer were characterized through the hydrodynamic volume, rather than the molecular weight, using the expression

$$[\eta] * M = M * (A + KM^\alpha) \tag{3}$$

which corresponds to that given by universal calibration[5,10,23] since, in SEC, the hydrodynamic volume determines the retention times. $[\eta] * M$ has the dimensions of cm$^3$ mol$^{-1}$ and is proportional to the mean solvated molecular volume $v_\epsilon$[10]:

$$[\eta] * M = 2.5 N_0 v_\epsilon \tag{4}$$

where $N_0$ is the Avogadro constant. The molecular size calculation can be applied to PEG oligomers, for which the intrinsic viscosity–molecular weight relationship is known. A calibration of the SEC columns is obtained in the form of a time of retention–molecular size relationship. Applying this relation to the SEC spectra for PF enables one to obtain the molecular size distribution of the PF in a given solvent system. Thus, a measure of the molecular size is obtained, enabling one to make size comparisons of the macromolecules in different solvents. This is not possible when calibration is conducted using $M$ only.

Specifically, using the MH parameters, or an empiric quadratic relation such as

$$\log[\eta] = A + B \log(M) + C \log(M)^2 \tag{5}$$

where $A$, $B$, and $C$ are constants (Table I), to calibrate the PEG molecular

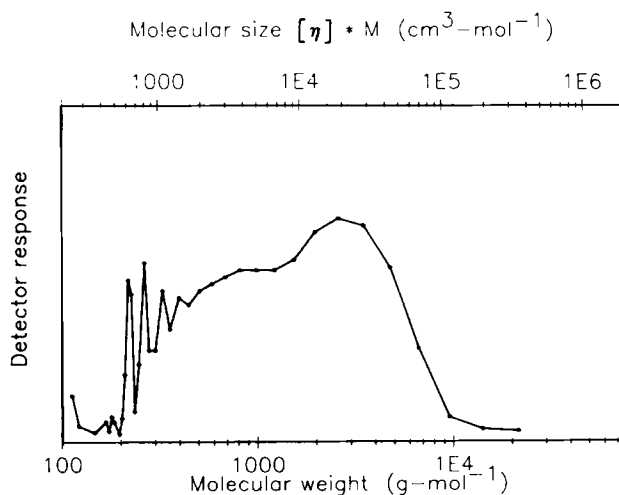Molecular size $[\eta] * M$ $(cm^3-mol^{-1})$



Fig. 3. Molecular weight and molecular size, $[\eta]$ $M$, distribution for a spray-dried resin in tetrahydrofuran with 0.4% trifluoroacetic acid at 25°C determined with Ultrastyragel 100 and 500 Å columns in series.

weights in terms of molecular size $[\eta]$, $([\eta]*M)$ values are calculated for the resols in the different solvent systems mentioned and a molecular size distribution is calculated form elution data. These are given for the same commercial spray-dried resol (Figs. 3–5) in THF/0.4% TCAA, DMF and DMF/0.1$M$ LiCl at 25°C. The molecular weight distribution of the resol is not given for pure THF solvent, since resols are not soluble in THF. Also, distributions are not provided for the water–borax NaOH buffer, since the resolution of the column used for such purposes was insufficient.[11] Number and weight molecular weight and molecular size averages are given in Table II for the resols. The

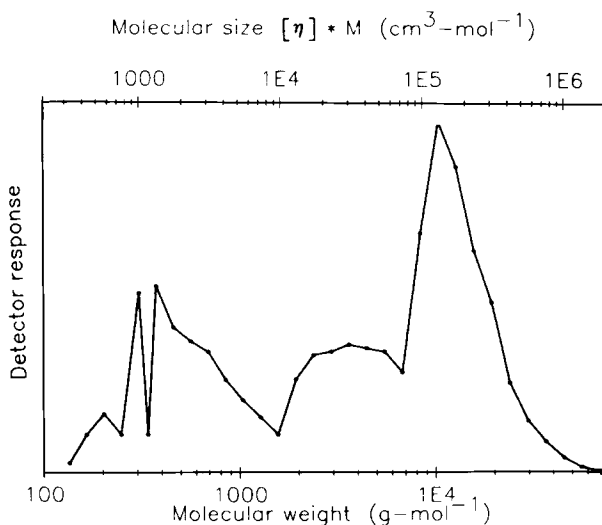Molecular size $[\eta] * M$ $(cm^3-mol^{-1})$



Fig. 4. Molecular weight and molecular size, $[\eta]M$, distribution of a spray-dried resin in $n,n$-dimethylformamide at 25°C determined with PLgel 50 and 500 Å columns in series.
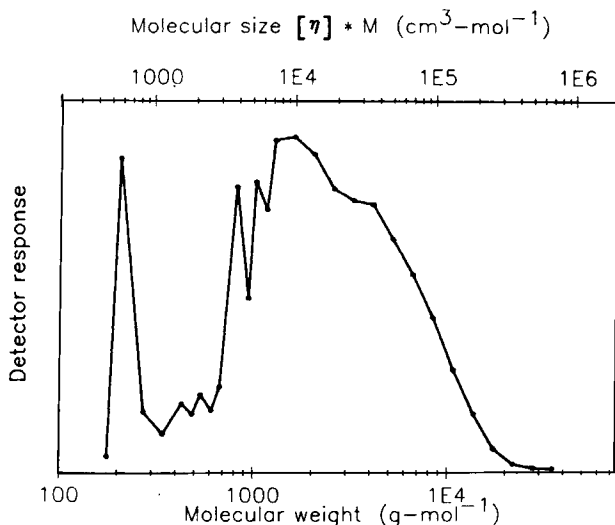
Molecular size $[\eta] * M$ $(cm^3 - mol^{-1})$



Fig. 5. Molecular weight and molecular size, $[\eta]M$, distribution for a spray-dried resin in $n,n$-dimethylformamide with $0.1m$ lithium chloride at 25°C determined with PLgel 50 and 500 Å columns in series.

molecular size averages were calculated in the same manner as for molecular weight, i.e.,

$$\left(\overline{[\eta] * M}\right)_n = \sum n_i [\eta]_i M_i \Big/ \sum n_i \tag{6}$$

$$\left(\overline{[\eta] * M}\right)_w = \sum n_i ([\eta] * M)_i^2 \Big/ \sum n_i [\eta]_i M_i \tag{7}$$

where $(\overline{[\eta] * M})_n$ is the number average molecular size and $(\overline{[\eta] * M})_w$ is the weight average molecular size. As in the case of the molecular weight averages, $(\overline{[\eta] * M})_n$ is the ratio of the first to the zeroth moment of the distribution, $(\overline{[\eta] * M})_w$, the ratio of second moment to the first, and the polydispersity index, $(\overline{[\eta] * M})_w/(\overline{[\eta] * M})_n$, the ratio of the second moment to the zeroth moment.[24]

Table II gives the number and weight average molecular size of a commercial spray-dried resol in four different solvent systems. The number molecular weight averages vary from 671 to 2180 and the weight number averages vary from 2910 to 6780, depending on the solvent/column system. The ratio of the apparent molecular weight averages for THF/TCAA and DMF/LiCl is approximately 3 to 1, i.e., PF is approximately three times larger in DMF/LiCl than in THF/TCAA, relative to PEG. The polydispersities are more informative, THF/TCAA and DMF/LiCl mixed solvents at 25°C give similar polydispersities while at 85°C DMF/LiCl gives a lower polydispersity and DMF a much higher polydispersity. Thus the resol in DMF/LiCl at 85°C could be the least aggregated while it would be most aggregated in DMF. However, some of these differences could be attributed to the differential solvation of the reference polymer in the solvents.

TABLE II
Number and Weight Averages of Molecular Weights and Hydrodynamic Volumes for Different Phenol–Formaldehyde Resin in Different Solvent Systems

| Solvent | Resin type | $\bar{M}_n$ | $\bar{M}_w$ | $\bar{M}_w/\bar{M}_n$ | $\overline{([\eta]*M)}_n$ | $\overline{([\eta]*M)}_w$ | $\overline{([\eta]*M)}_w/\overline{([\eta]*M)}_n$ |
|---|---|---|---|---|---|---|---|
| THF/TCAA | Spray-dried | 6.71E2[a] | 2.91E3[a] | 4.3[a] | 2.01E3 | 3.62E4 | 18 |
| DMF | Spray-dried | 1.52E3[a] | 1.19E4[a] | 7.8[a] | 5.58E3 | 5.10E5 | 91 |
| DMF/LiCl | Spray-dried | 1.97E3 | 6.78E3 | 3.4 | 1.05E4 | 2.31E5 | 22 |
| DMF/LiCl 85°C | Spray-dried | 2.18E3[a] | 4.40E3[a] | 2.0[a] | — | — | — |
| THF/TCAA | Normal cook | 3.35E2 | 1.86E3 | 5.5 | 7.71E2 | 2.17E3 | 28 |
| THF/TCAA | Freeze-dried | 3.43E2 | 1.42E3 | 4.1 | — | — | — |
| THF/TCAA | Freeze-dried[b] | 4.19E2 | 2.04E3 | 4.9 | — | — | — |

[a] These data are already published.[11]
[b] Kept at 5°C 6 months after freeze-drying.

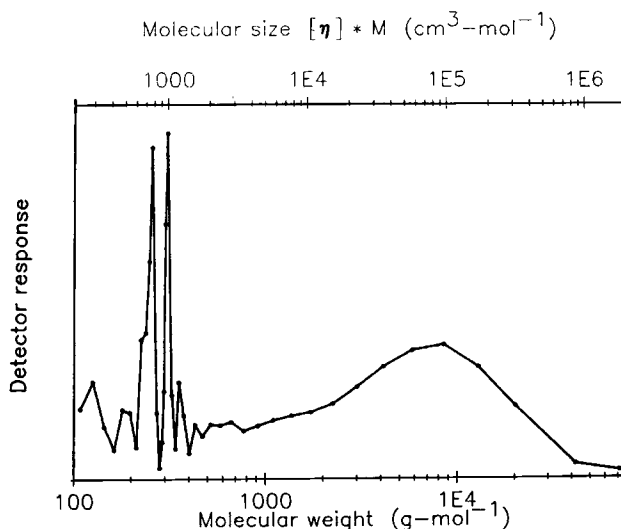Molecular size  $[\eta]$ * M  $(cm^3\text{-}mol^{-1})$



Fig. 6.  Molecular size distribution of a 50/50 mixture of high molecular weight and a low molecular weight resol.

The number average molecular size, $(\overline{[\eta]*M})_n$, varies between 2.01E3 to 5.58E3 cm$^3$ mol$^{-1}$ and the weight average molecular size between 3.62E4 to 5.10E5 cm$^3$ mol$^{-1}$. The ratio of the molecular dimension averages in DMF/LiCl and in THF/TCAA is about 5 to 1. This is the real ratio between the molecular sizes in both solvents and is not dependent on the differential solvation of PEG. The molecular size polydispersity in both solvent is about 20 to 1. The polydispersity in DMF at 25 is very high (91), which indicates aggregation.

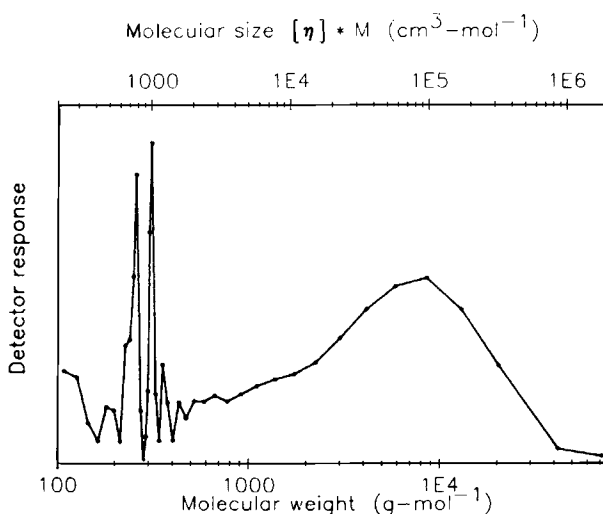Molecular size  $[\eta]$ * M  $(cm^3\text{-}mol^{-1})$



Fig. 7.  Calculated (synthetic) molecular size distribution for a liquid resin made up of a 50/50 mixture of a high molecular weight and a low molecular weight resol, as in Figure 6.

The molecular size distribution of the PF in THF/TCAA (Fig. 3) is similar to the distribution determined in DMF/LiCl (Fig. 5), with the latter being a better solvent. This is especially so for low molecular weight species, equivalent to a PEG molecular weight of 200–300. The resol in DMF at 25°C gives a much larger average molecular size, and a bimodal distribution which indicate some form of aggregation. This confirms that the presence of TCAA or LiCl discourages this aggregation. This can be verified by combining in a computer the SEC spectra of a low and a high molecular weight resol and comparing with the SEC spectra of the actual mixture. The match is reasonably good for a 50/50 low/high mixture, as shown in Figures 6 and 7.

Interestingly, Tobiason et al.[25] has shown that the MH parameters of PF resols in $1N$ NaOH or DMF are very similar ($\alpha$ of 0.48 and 0.51, respectively). This means that the molecular size distribution in $1N$ NaOH would be as shown in Figure 4, for DMF as solvent. Resols, when used as liquid adhesives in the waferboard industry, are in the form of a 50% aqueous solution with a high concentration of NaOH. Thus the mentioned distribution approximates that of the resol initially in contact with wood, as an aqueous solution.

### Molecular Size and Weight of Different Resols

Figures 3 and 8 give the molecular weight and dimension distributions of a spray-dried and liquid resol, respectively (solvent: THF/TCAA). The liquid resol (typical formulation) has a lower average molecular weight and its polydispersity is higher, as seen in Table II.

It is important to compare the resols, in powder or liquid form, soon after their synthesis, or at least to keep the samples at low temperatures (below $-10°C$), since polymerization will still proceed in refrigerated samples, albeit very slowly. As shown in Table II molecular weights of refrigerated samples increased significantly over a 6-month long storage in a refrigerator.
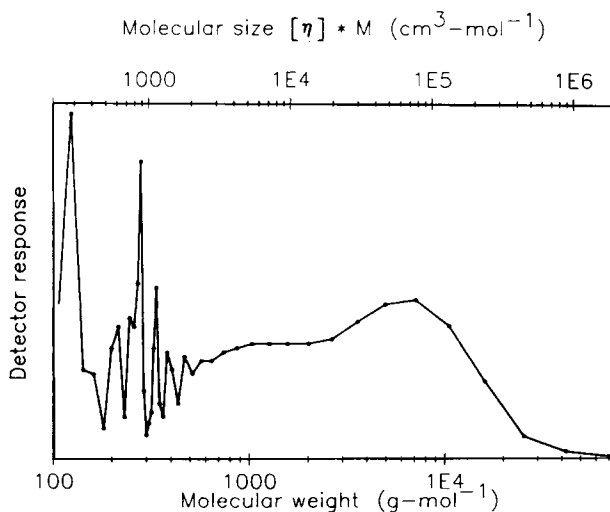


Fig. 8.   Molecular weight and molecular size distribution for a liquid resin.

It is known that macromolecules below a certain critical size can penetrate wood materials[26] whereas molecules with a molecular size larger than that of PEG of MW 3000, which has a radius of giration of 18–20 Å, cannot diffuse into wood substrates. It is not possible to be more definite since caustic solutions, in concentrations such as used in resols, swell wood and change its pore structure. Following the molecular size distribution in Figure 4, about a third to half of the resin would be able to penetrate the cell walls of a wood substrate. A low molecular weight resin (with the highest molecular weight lower than that equivalent to PEG 3000) results in a "starved" bond, when all the resin penetrates into the wood. If all molecular weight fractions are of larger size than that equivalent to PEG 3000 poor adhesion also results, due to insufficient adhesive penetration.

## CONCLUSION

The molecular weight and molecular dimension distribution has been measured for several resols in different solvent systems. The effects of salts in solution is to decrease the apparent molecular weight and size by limiting aggregation. Inasmuch as one uses a solvent system which does not promote aggregation, molecular weight distributions may still be useful for comparison of resols, but for more general use, molecular size distributions and averages are more meaningful.

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